Journal of Molecular Spectroscopy 267 (2011) 108–111

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

# Rotational spectroscopy of lutetium monoxide, LuO

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ARTICLE INFO

*Article history:*
Available online 26 February 2011

*Keywords:*
Lutetium monoxide
Fourier transform microwave spectroscopy
Internuclear distance
Rotational spectrum
Spectroscopic constants
Astrophysical search

ABSTRACT

The pure rotational spectrum of $^{175}Lu^{16}O$ in its ground electronic state ($X^2\Sigma^+$) has been observed with a cavity pulsed jet Fourier transform microwave spectrometer. The samples were prepared by laser ablation of Lu metal in the presence of gaseous oxygen, and stabilized in pulsed jets of Ar. The $N = 1–0$ transition has been measured in the $v = 0$, 1 and 2 states. All the observed lines show Zeeman splittings caused chiefly by the Earth's magnetic field. The transitions show effects of electron spin-rotation structure and of $^{175}Lu$ hyperfine structure. Several hyperfine parameters have been evaluated, and are interpreted in terms of the molecular electronic structure. An improved equilibrium internuclear distance, $r_e$, is presented. The results should facilitate astrophysical searches for the molecule.



## 1. Introduction

A spectrum of lutetium oxide, LuO, was first reported in 1911 [1], and there were several reports over the next few decades of electronic spectra at vibrational resolution [2–6]. The first studies at rotational resolution were reported in the early 1970s [6]. Bacis and Bernard [7] gave a detailed account of a rotational analysis of a $\Sigma^+–\Sigma^+$ transition, and noted that the lower state, presumably the ground electronic state, followed Hund's case ($b_{\beta S}$) coupling. For it they presented values for the rotational constant, the centrifugal distortion constant and a Fermi contact parameter $b$ for $^{175}Lu$. In 1986 Bernard and Effantin [8] published a much more extensive analysis of three bands. They verified the earlier identification of the ground electronic state, $X^2\Sigma^+$, and obtained more precise values for its spectroscopic constants, extending the analysis to include both the ground and first excited vibrational states. They also evaluated its equilibrium internuclear distance, $r_e$. A matrix isolation infrared spectrum of LuO has recently been reported [9].

LuO is also of interest from other perspectives. For example, Lu has been observed in the solar spectrum [10], and in the metal-poor galactic halo stars CS22892-052 [11] and CS31062-050 [12]. Thus, spectral features of LuO are of interest for identifying the presence of rare earth oxides in star atmospheres and the interstellar medium. LuO has also attracted attention from researchers studying the lanthanide contraction and developing basis sets for the lanthanides [13].

The present paper reports the first observed pure rotational spectrum of LuO. It was prepared using laser ablation, and studied in its ground ($X^2\Sigma^+$) electronic state by Fourier transform microwave (FTMW) spectroscopy. More precise values of previously determined constants have been obtained along with values for several previously unmeasured parameters. A more precise equilibrium internuclear distance has been obtained. $^{175}Lu$ hyperfine parameters have been interpreted in terms of the molecular structure. The results should facilitate astrophysical searches for the molecule.

## 2. Experimental methods

The spectra were obtained with the Balle–Flygare-type [14] cavity pulsed jet FTMW spectrometer and laser ablation system described in detail earlier [15,16]. In brief, the cell was a Fabry–Perot cavity consisting of two spherical Al mirrors 38.4 cm radius of curvature, 24 cm in diameter and approximately 30 cm apart. One mirror was fixed and the other movable to tune the cavity resonant frequency. A pulsed nozzle (General Valve Series 9) was mounted in the fixed mirror; from it samples entrained in supersonic jets of noble gas were injected into the cavity. The two main advantages of this technique were: (i) in the jets the samples were in a collision-free environment, and thus stabilized, and (ii) the rotational temperature was near 1 K, so that only the lowest rotational levels were populated, with consequent increase in spectral intensity. In addition, the lines were doubled by the Doppler effect; the rest frequency was the average of those of the two Doppler components. The microwave source was referenced to a Loran C Frequency Standard accurate to 1 part in $10^{10}$.

A 5 mm diameter Lu rod (HEFA Rare Earth Canada) was mounted 5 mm from the nozzle orifice in a stainless steel nozzle cap, and irradiated with the fundamental of a pulsed Nd:YAG laser

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0022-2852/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2011.02.017

(1064 nm) [16]. The resulting Lu plasma reacted with $O_2$ (1% in ~6 atm Ar backing gas) and the reaction products were injected into the cavity in the Ar supersonic jet. A 5 mm diameter lanthanum (La) rod (Alfa AESAR) was used in experiments to assist in line assignments of LuO.

## 3. The spectrum, and its assignment and analysis

Since the ground electronic state of LuO is $X^2\Sigma^+$, the molecule is paramagnetic with one unpaired electron. According to the electronic spectrum, the coupling of the electron spin (**S**) and $^{175}$Lu nuclear spin (**I**) angular momenta is very strong, and much stronger than the coupling of either with the molecular rotation (**N**). The coupling scheme is therefore Hund's case ($b_{\beta S}$):

$$\mathbf{S}+\mathbf{I}=\mathbf{G}$$

$$\mathbf{N}+\mathbf{G}=\mathbf{F}$$

Given that the quantum number $S = ½$ and for $^{175}$Lu $I = 7/2$, the quantum number $G = 3$ or 4. $G$ is always a good quantum number, so states with different values of $G$ do not mix.

Only the transition $N = 1–0$ was observable in the frequency range of our spectrometer. The values of the quantum number $F$ are:

$$\text{for } G=3:\ N=1,\ F=2,3,4;\quad N=0,\ F=3,\ \text{and}$$

$$\text{for } G=4:\ N=1,\ F=3,4,5;\quad N=0,\ F=4.$$

From the selection rules $\Delta G = 0$; $\Delta F = 0, \pm 1$, the transition should have six hyperfine components. Contributions to their frequencies come from, besides the rotational constant $B$ and the centrifugal distortion constant $D_J$, the Fermi contact interaction ($b_F$), the nuclear spin-electron spin dipole–dipole interaction ($c$), the electron and nuclear spin-rotation interactions ($\gamma$ and $C_I$, respectively), and $^{175}$Lu nuclear quadrupole coupling ($eQq(^{175}\text{Lu})$). Values for the rotational constant, distortion constant and a Fermi contact parameter were available from the literature [8]. Although this information indicated a general search range, details of the assignment needed to be worked out.

Searches were carried out in the frequency region 20.4–22.3 GHz, as predicted from the known $B$ value. Many transitions were found which could be attributed to $^{175}$Lu$^{16}$O, presumably in the ground and excited vibrational states. Each transition was a group of Zeeman components resulting from the interaction of the electron spin with the Earth's magnetic field (plus possible small extraneous fields in the laboratory). The line width of each component was 7–10 kHz fwhm. We were unable to collapse these groups to single lines because the spectrometer was not equipped with Helmholtz coils to cancel the external field. However the Zeeman patterns were different for different lines, and gave us major clues about their assignments.

It might have been possible to assign the transitions knowing the relative directions of the external magnetic field and the microwave electric field. Since the former was unknown, an alternate tactic was adopted. The assignment of $N = 1–0$ of lanthanum monoxide (LaO, not LuO!) is known [17]. Since the ground state of LaO is also $X^2\Sigma^+$, $I(^{139}\text{La})$ is also 7/2, and the coupling scheme is also case ($b_{\beta S}$), the magnetic properties of the two molecules are very close. Since we had available a rod of La metal, each of the six transitions of $N = 1–0$ for LaO was recorded, and their Zeeman patterns were compared to those of the strongest transitions of LuO. The comparison is shown in Fig. 1. Initially only 5 transitions of LuO (those numbered 1, 2, 3, 4, 6 in Fig. 1) were available. It was clear from the Zeeman patterns that numbers 1 and 6 should be assigned to $G,F = 4,5–4,4$ and 3,2–3,3, respectively. Similarly, number 2 was either $G,F = 4,4–4,4$ or 3,3–3,3. A series of fits of these five lines was carried out to five constants, as defined below, with $D_J$ set to its literature value [8], and $C_I(^{175}\text{Lu})$, the smallest constant, set to zero. In these fits, transitions 1 and 6 were given the above assignments, transition 2 was given one of its two likely assignments, and transitions 3 and 4 were assigned to $G,F = 4,3–4,4$ or 3,4–3,3. For an assignment to be considered plausible it had to reproduce $b$ ($=b_F - c/3$) from the electronic spectrum; it also had to predict accurately the missing sixth transition with a reasonable

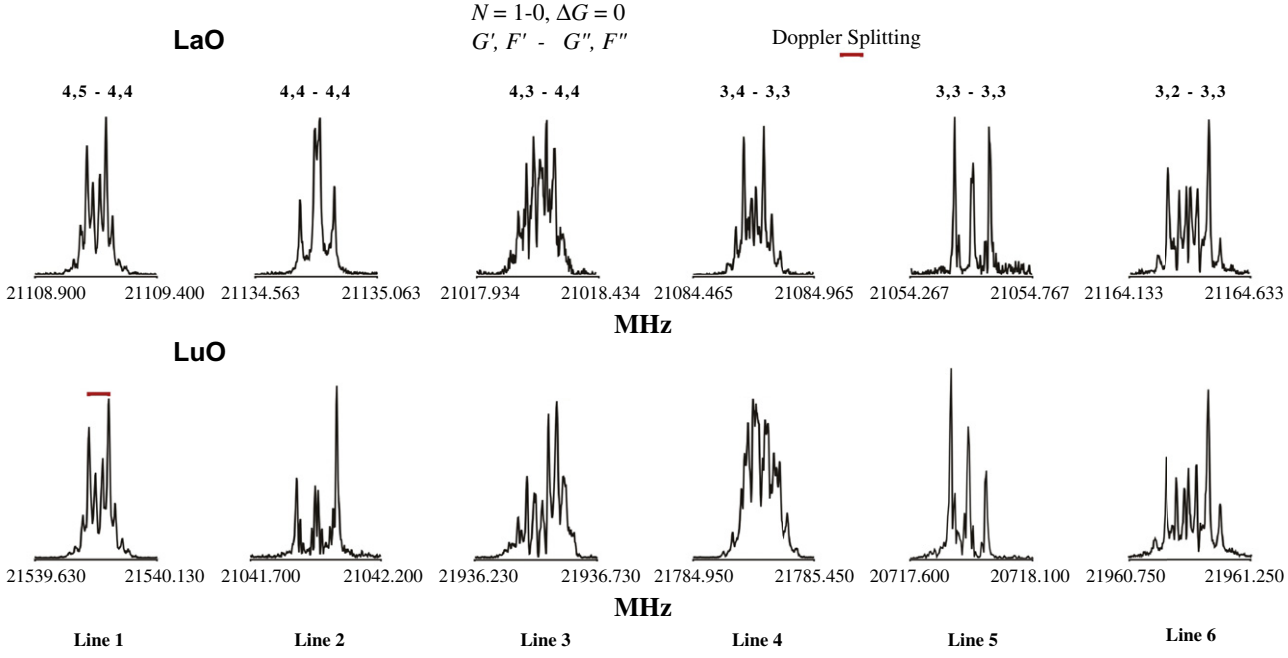


**Fig. 1.** The six $N = 1–0$ transitions of $^{175}$LuO in the $v = 0$ state of its $X^2\Sigma^+$ electronic state, along with their $G',F' - G'',F''$ assignments. Each transition is resolved to several Zeeman components by chiefly the Earth's magnetic field. To facilitate assignments each transition is compared with the corresponding transition of LaO [17]. The criteria for making the assignments are given in the text. The Doppler splitting of each component of the transitions is given in red at the top of the figure; an example is given for line 1 of LuO. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)